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Review article

Research progress on the raw and modified montmorillonites as adsorbents for mycotoxins: A review

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A B S T R A C T

Mycotoxin, as one of the most common pollutants in animal feeds, is harmful and widespread, which has severely restricted the healthy development of livestock and feed industries. Therefore, to remove mycotoxins from animal feeds is becoming an intractable problem. Currently, naturally occurred clay minerals, especially montmorillonite (Mt), have been considered as promising adsorbents for high-efficient removal of toxic mycotoxins from animal feeds because they are eco-friendly, low-cost, and highly efficient for adsorption of mycotoxin. It is important to timely summary the latest researches, which helps the followers to develop or exploit other new adsorbents for mycotoxins. Thus, this review intensively summarized the latest research progress on raw Mt and the modified ones as adsorbents for mycotoxins, and especially on the adsorption mechanism. In addition, the future applications of Mt as adsorbents for removal of mycotoxins were discussed.

1. Introduction

Mycotoxins are secondary metabolites produced by some fungal species, which are always formed during growth, harvesting, drying or storage of fruits, seeds or grains (Kabak et al., 2006). Until now, approximate 400 kinds of mycotoxins have been detected. Among them, aflatoxins, ochratoxins, deoxynivalenol, zearalenone and fumonisins have received much attention because of their frequent occurrence in feeds and severe toxic effect on animals and humans (Verheecke et al., 2016) (Table 1). On the one hand, the occurrence of mycotoxins in feeds may destroy or reduce the nutritional value and palatability of feeds, and thus make the animals refuse to eat, grow slower, fall ill easily, and even die (Huwig et al., 2001). On the other hand, mycotoxins may transfer to human body through food chain, such as milk, eggs and other products, which will cause severe threat to human health (Sforza et al., 2006; Molina-Molina et al., 2014; Escrivá et al., 2015; Ferre, 2016). In a word, mycotoxin has seriously hampered the healthy development of livestock and feed industries, so practical and effective methods for removal of mycotoxins from animal feeds are in great demand (Scudamore, 2005; Ferre, 2016).

Many number of approaches such as physical, chemical and biological methods, have been used to remove, destroy or reduce mycotoxins (Hwang and Lee, 2006; Amezqueta et al., 2008). In general, physical approaches include heat inactivation, irradiation (ultraviolet light or gamma radiation), and solvent extraction, etc. (Méndez-Albores et al., 2004; Fandohan et al., 2005; Markov et al., 2015); Chemical methods usually rely on a large number of chemical agents including acids, bases and oxidizing agents, to react with mycotoxins and convert them to non-toxic or less toxic compounds (Elias-Orozco et al., 2002; Méndez-Albores et al., 2007; Amezqueta et al., 2008); Biological methods usually rely on various microorganisms, such as yeasts, actinomycetes and algae, to degrade mycotoxins and convert them to non-toxic or less toxic compounds (Nesci et al., 2005; Palumbo et al., 2006; Fazeli et al., 2009; Jermnak et al., 2013); Overall consideration, all these approaches are effective to mycotoxins to a certain degree, but they still have considerable limitations in practical applications. For instance, physical method is expensive and harsh temperature may produce undesirable changes to feeds and foods despite high temperature can decompose aflatoxins. Chemical method may significantly alter or destroy the nutritional value and palatability of feeds and produce or leave toxic carcinogenic and mutagenic residues in the final products, which are harmful to animals (Méndez-Albores et al., 2007). In terms of biological methods, some limitations such as long degradation time, incomplete degradation and culture pigmentation may restrict their applications of

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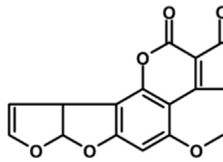
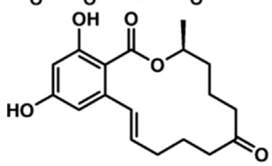
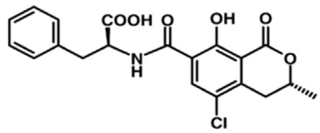
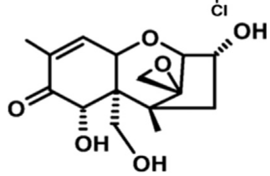
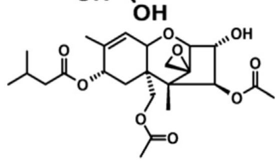
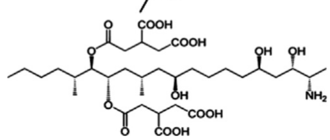
Table 1
Structure and molecular formula of the major mycotoxins in feeds.

Mycotoxins	Structure formula	Molecular formula	Ref.
AFB_1		$C_{17}H_{12}O_6$	Richard (2007), Chaytor et al. (2011)
ZEA		$C_{18}H_{22}O_5$	Chaytor et al. (2011)
OTA		$C_{20}H_{18}ClNO_6$	Chaytor et al. (2011)
DON		$C_{15}H_{20}O_6$	Richard (2007), Chaytor et al. (2011)
T-2 toxin		$C_{24}H_{34}O_9$	Richard (2007)
FB_1		$C_{34}H_{59}NO_{15}$	Hove et al. (2016)

AFB_1, Aflatoxin B_1; ZEA, Zearalenone; OTA, Ochratoxin A; DON, Deoxynivalenol; FB_1, Fumonisins B_1.

biological methods in feed and food industries. Recently, adsorption approach is proving to be a more suitable option for the treatment of mycotoxins. A variety of adsorbents, such as activated carbon, clay minerals and resin, have been used to bind and immobilize mycotoxins for preventing or reduce reducing their harmful effects on to livestock. By comprehensive comparison, adsorption method involves both of chemical force and physical force, which can not only effectively reduce the toxic impact of mycotoxins, but also avoid toxic residues, and becomes the most widely applied way to protect animals against mycotoxins. Nonetheless, various mycotoxins may occur simultaneously in animal feeds (Broggi et al., 2007; Sun et al., 2011; Madbouly et al., 2012), and the toxic effects of any mycotoxins may be amplified due to the synergistic interaction with other mycotoxins. Therefore, to choose and develop efficient adsorbents becomes rather difficult.

At present, various types of adsorbents, e.g., yeast cell wall components (Tanpong et al., 2017), synthetic polymers (cholestyramine, polyvinylpyrrolidone) (Avantaggiato et al., 2003, 2005), humic substances (Sabater-Vilar et al., 2007), dietary fibers (Aoudia et al., 2008, 2009), clay minerals (Jiang et al., 2010, 2012a,b; Santos et al., 2011) and activated carbons (Diaz et al., 2002; Sabater-Vilar et al., 2007), have been extensively studied for the adsorption of different types of mycotoxins. Among them, clay minerals, as the materials in "greening 21st century material worlds", have attracted more attention owing to their excellent adsorption performance, high chemical stability and biocompatibility advantages. Moreover, clay minerals are naturally abundant, green, non-toxic and low-cost. Common clay minerals including Mt, kaolinite and halloysite, etc., are turning out to be effective adsorbents for mycotoxins. For instance, the toxic effect of aflatoxin on poultry was effectively restrained by adding 0.5 wt% of Mt to aflatoxin contaminated diet (Bailey et al., 2006). In addition, the born alive litter weight and litter weaned weight improved by 29.3 and 56.0%, respectively by adding 1.0 wt% of modified halloysite nanotubes to ZEA contaminated diet (Zhang et al., 2015). Among these clay minerals, Mt and its modification products have been extensively studied for their congenital structural advantage and adsorptive characteristics. It is of importance to timely summary and concise the relevant research progress, which is conducive to inspire new ideas and promote the development of new products. Therefore, this paper reviewed the latest research progress on raw and modified Mt as adsorbents for mycotoxins, and on describing the various adsorption mechanisms. It is expected that this review can provide a certain reference for the research and development of efficient adsorbents of mycotoxins.

2. Removal of mycotoxins by Mt

Mt is the main component of bentonite (Bergaya and Lagaly, 2013). It has a 2:1 configuration with two silicate tetrahedrons sandwiching an aluminum-oxygen octahedron (Fig. 1) (Zhu et al., 2016). The replacement of Al^{3+} ions for Mg^{2+} or Fe^{2+} ions in the octahedral sheets leads to the charge imbalances in Mt, so that exchangeable cations and interlayer water molecules are present between the 2:1 layers for charge compensation (Nones et al., 2015c; Zhu et al., 2016). Owing to the special structure features, the physical and chemical properties of Mt is easy to be controlled and improved by moderate modification with different modifiers or techniques (Dékány et al., 1978; Nagy et al., 2013). Indeed, the introduction of different types of inorganic cations,